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# Convective hydrothermal CO<sub>2</sub> emission from high heat flow regions

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#### Abstract

In addition to volatiles released from volcanoes, the flux of  $CO_2$  to the atmosphere from other sources (e.g., metamorphism and subsurface magmatism) represents an important aspect of the global carbon cycle. We have obtained a direct estimate of the present-day atmospheric  $CO_2$  flux from convective hydrothermal systems within subaerial, seismically-active, high heat flow regions. Geothermal systems of the Salton Trough (California, U.S.A.) and the Taupo Volcanic Zone (New Zealand) provide benchmarks for quantifying convective hydrothermal  $CO_2$  fluxes from such regions.  $CO_2$  fluxes from the Salton Trough ( $\sim 10^9$  mol yr<sup>-1</sup>) and the Taupo Volcanic Zone ( $\sim 8\cdot 10^9$  mol yr<sup>-1</sup>) were computed using data on convective heat flow and the temperatures and  $CO_2$  concentrations of reservoir fluids. The similarity in specific  $CO_2$  flux ( $\sim 10^6$  mol km<sup>-2</sup> yr<sup>-1</sup>) from these two disparate geologic/tectonic settings implies that this flux may be used as a baseline to compute convective hydrothermal  $CO_2$  emission from other areas of high heat flow. If this specific flux is integrated over high heat flow areas of the circum-Pacific and Tethyan belts, the total global  $CO_2$  flux could equal or exceed  $10^{12}$  mol yr<sup>-1</sup>. Adding this flux to a present-day volcanic  $CO_2$  flux of  $\sim 4\cdot 10^{12}$  mol yr<sup>-1</sup>, the total present-day Earth degassing flux could balance the amount of  $CO_2$  consumed by chemical weathering ( $\sim 7\cdot 10^{12}$  mol yr<sup>-1</sup>).

#### 1. Introduction

Because of the  $CO_2$  greenhouse effect, controls on atmospheric  $CO_2$  content are of particular interest. Assuming a steady-state global carbon cycle, Berner (1991, 1992) equated the global magmatic and metamorphic  $CO_2$  degassing flux to the atmosphere with the  $CO_2$  consumed (6.7·10<sup>12</sup> mol yr<sup>-1</sup>) by chemical weathering of silicates. Volcanic  $CO_2$  (released from volcanoes) has been estimated to be  $\sim 4 \cdot 10^{12}$  mol yr<sup>-1</sup>

which is insufficient to balance the global carbon cycle (Gerlach, 1991, 1993). CO<sub>2</sub> degassing of subsurface magmas and metamorphic decarbonation could make up the deficit.

This paper is an outgrowth of Kerrick and Caldeira's (1993, 1994) research on the paleoclimatic consequences of metamorphic CO<sub>2</sub> degassing. In light of the uncertainties in estimating CO<sub>2</sub> fluxes by indirect methods (Berner et al., 1983; Berner, 1991, 1992), they emphasized the need for direct estimates of the present-day global non-anthropogenic CO<sub>2</sub> emission. In this paper we focus our attention on subaerial CO<sub>2</sub>

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emission arising from convective hydrothermal circulation in regions of high heat flow. We exclude CO<sub>2</sub> emission from volcanoes (cf. S.M. Williams et al., 1992) and from biotic and anthropogenic sources.

Areas of abundant convective hydrothermal CO<sub>2</sub> emission share several geologic similarities, i.e. high heat flow, recent volcanism and seismically-active extensional tectonic regimes. CO<sub>2</sub> springs are abundant in the circum-Pacific and Tethyan orogenic belts (Barnes et al., 1978, 1984). Based on isotopic and chemical parameters of the spring effluents, Barnes et al. (1978, 1984) concluded that much of this CO<sub>2</sub> originates from active metamorphism. Within these orogenic regions, we quantified CO<sub>2</sub> fluxes from selected "case study" geothermal areas. These areas represent contrasting tectonic/geologic regimes and thus provide an opportunity to evaluate the effect of different geologic settings on CO<sub>2</sub> emission. In evaluating the genesis of CO<sub>2</sub> emitted from geothermal systems we considered the relative contributions of magmatic vs. metamorphic mechanisms and also mantle vs. crustal CO<sub>2</sub> sources. We emphasize that our computations of magmatic volatiles exclude emission from volcanoes (cf. S.M. Williams et al., 1992); thus, our treatment of magmatic volatiles is confined to degassing of subsurface magmas.

Of the geothermal environments world wide, the Salton Trough (California, U.S.A.) and the Taupo Volcanic Zone (New Zealand) have the most comprehensive available data bases for computing convective hydrothermal CO<sub>2</sub> emission. CO<sub>2</sub> fluxes from geothermal systems in the Salton Trough (ST) and Taupo Volcanic Zone (TVZ) were computed using data on *convective* heat flow (Garg and Kassoy, 1981) coupled with the temperatures and CO<sub>2</sub> concentrations of reservoir fluids. Correlation between heat flow and advective flux of fluids to the surface is justified in that the bulk of the heat loss in geothermal systems occurs through the surface dispersal of vapor and hot water (Henley, 1985). In the ST an independent estimate of CO<sub>2</sub> flux can also be obtained from isotopic compositions of the surface discharges and mass balance of CO<sub>2</sub> loss by metamorphic decarbonation (McKibben and Williams, 1995).

#### 2. Taupo Volcanic Zone (TVZ)

The TVZ (Fig. 1) represents a volcanic arc and back-arc basin associated with subduction of the Pacific plate below the Australian plate. The TVZ contains 20 known geothermal systems occurring in a graben-type structure developed within an extensional regime. The volcanic arc in the southeastern half of the TVZ consists primarily of dacite-andesite volcanics, whereas the backare basin dominantly contains the products of silicic (rhyolitic-dacitic) volcanism (Cole, 1990). Several large calderas (Fig. 1; Brown et al., 1994) mark major eruptive centers in the back-arc basin. The TVZ has experienced extensive recent volcanism — the 186 AD Plinian eruption from the Taupo caldera was particularly large and violent.

For many of the TVZ geothermal systems, surface emission of volatiles is marked by hot springs, mud pots and fumaroles. Isotopic data and B-He-Ar-CO<sub>2</sub>-N<sub>2</sub> chemical signatures (Giggenbach et al., 1993) are compatible with a magmatic origin for CO<sub>2</sub>. Giggenbach (1992) concluded that CO<sub>2</sub> originated from degassing of andesitic melts and that the magmatic volatiles were derived by devolatilization of subducted sediments. Metamorphic devolatilization may have triggered anatexis in the overlying mantle (as implied by Giggenbach, 1992, fig. 4); thus, as considered by Berner et al. (1983), much of the CO<sub>2</sub> released from the TVZ and other geothermal systems within volcanic arcs (Marty and Jambon, 1987; Giggenbach, 1992; Varekamp et al., 1992) may arise from metamorphic degassing.

The elevated heat flow measured over the hydrothermal systems mainly arises from fluid convection rather than conduction (Garg and Kassoy, 1981). We assume that CO<sub>2</sub> remains dissolved in the single-phase convecting fluids until near-surface depths (i.e. upper few km) are reached (Henley, 1985), such that there is a direct relation between heat flow and CO<sub>2</sub> flux from

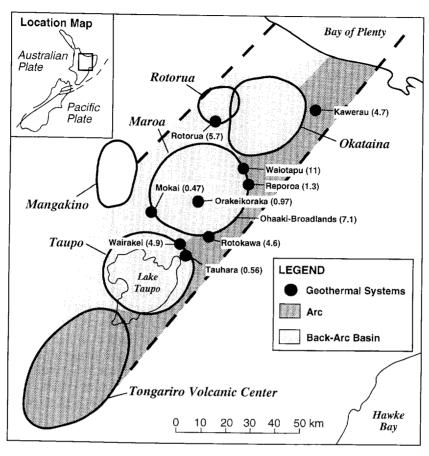


Fig. 1. The Taupo Volcanic Zone showing locations of the geothermal systems used for  $CO_2$  flux calculations (location on North Island of New Zealand is shown in inset map) and five major volcanic centers (calderas) (modified from Cole, 1990). The number adjacent to the name of each geothermal system is the yearly  $CO_2$  flux  $\times 10^8$  (e.g., the flux is  $7.1 \cdot 10^8$  mol yr<sup>-1</sup> for the Ohaaki–Broadlands geothermal system).

the reservoir. As reviewed by Seward et al. (1993) and detailed by Seward and Kerrick (1995), the  $CO_2$  flux from each TVZ geothermal system was computed by combining data on convective heat flow with the temperature and  $CO_2$  concentration of deep reservoir fluids. Available data allow  $CO_2$  fluxes to be calculated for ten geothermal systems (Fig. 1; Table 1). The approximate surface perimeter of each of the TVZ geothermal systems is delineated by the 10–20- $\Omega$ -m electrical resistivity contour. For each system, the total surface heat flow data (in MW) were obtained by methods outlined by Dawson (1964) and Elder (1981). Available well head output data are summarized by Allis (1981) and

Stern (1987). Down-hole reservoir temperatures have been directly measured. The composition of the reservoir effluents has been determined by chemical analysis of the gas and liquid that are discharged from cyclone separators at well heads. The composition of the deep homogeneous (single phase) reservoir fluid is calculated from the CO<sub>2</sub> contents of both liquid+gas discharged from wells. Using the average reservoir temperatures, enthalpy is derived from the steam tables (Haar et al., 1984) by assuming that the enthalpy of the homogeneous fluid is equivalent to that of liquid water along the liquid-vapor equilibrium for pure H<sub>2</sub>O. Use of data for pure H<sub>2</sub>O is justified in light of the relatively low

Table 1 Summary of data (heat flow, temperature, CO<sub>2</sub> content) and CO<sub>2</sub> fluxes for geothermal systems of the Taupo Volcanic Zone<sup>a</sup>

System	Heat flow (MW)	T (°C)	$CO_2$ (mol kg $^{-1}$ )	Flux $(10^8 \text{ mol yr}^{-1})$
Kawerau	100	300	0.2	4.7
Mokai	100	300	0.02	0.47
Ohaaki/Broadlands	100	300	0.3	7.1
Orakeikorako	340	250	0.01	0.97
Reporora	45	250	0.1	1.3
Rotorua	400	250	0.05-0.1	5.7
Rotokawa	210	320	0.10	4.6
Tauhara	100	300	0.02	0.56
Waiotapu	500	300	0.1	11
Wairakei	400	260	0.04	4.9

Total CO<sub>2</sub> flux  $\approx 4.1 \cdot 10^9$  mol yr<sup>-1</sup>.

salinities of the fluids discharged from the TVZ geothermal systems. Converting convective heat flow from MW to J s<sup>-1</sup>, the CO<sub>2</sub> flux (F) for each geothermal system is computed from:  $F = (W/H) \times m$ , where W = heat flow (J s<sup>-1</sup>), H = enthalpy (J g<sup>-1</sup>) and m = molality of CO<sub>2</sub>.

CO<sub>2</sub> fluxes for the TVZ geothermal systems (Fig. 1) range from  $0.47 \cdot 10^8$  mol yr<sup>-1</sup> (Mokai) to  $11 \cdot 10^8$  mol yr<sup>-1</sup> (Waiotapu). Many of the geothermal systems with the highest CO<sub>2</sub> fluxes are located in the volcanic arc. This may suggest that recent subsurface magmatism is concentrated beneath the volcanic arc (Giggenbach et al., 1993). The geothermal systems considered here probably represent a reasonable ensemble from the volcanic arc and back-arc basins (Fig. 1). Thus, the total CO<sub>2</sub> flux of  $\sim 4 \cdot 10^9$  mol yr<sup>-1</sup> from the ten systems shown in Fig. 1 should not be biased toward low-CO<sub>2</sub> or high-CO<sub>2</sub> systems. The size and reservoir characteristics of the remaining 10 known TVZ geothermal systems appear to be similar to those considered for our CO<sub>2</sub> flux calculations. Thus, if the total CO<sub>2</sub> flux from the remaining ten TVZ geothermal systems is similar to the total flux of the systems shown in Fig. 1, the total CO<sub>2</sub> flux from all known geothermal systems in the TVZ could approach 10<sup>10</sup> mol  $vr^{-1}$ .

CO<sub>2</sub> emanating from many western circum-Pacific geothermal systems (i.e., New Zealand to Japan) appears to be dominantly of magmatic origin (Hedenquist, 1992). However, in the high heat flow areas of western and southern California, and in some geothermal systems in Central America (Janik et al., 1991), considerable CO<sub>2</sub> may be of non-magmatic origin. The Salton Trough provides a particularly well-studied example of a circum-Pacific geothermal system with CO<sub>2</sub> dominantly of metamorphic origin.

#### 3. Salton Trough (ST)

The ST geothermal systems are developed within a sequence of Pliocene and Pleistocene clastic sediments deposited by the Colorado River. Recent volcanism, high heat flow and seismicity are compatible with the hypothesis that the ST represents an active spreading center that is the landward continuation of the East Pacific Rise (A.E. Williams and McKibben, 1989). Each of the high-temperature geothermal systems within the central ST is a plume of convectively circulating fluid of known composition (A.E. Williams and McKibben, 1989). Stable isotope data indicate that the water in the geothermal fluids is predominantly of evolved meteoric origin. However, CO<sub>2</sub> is largely derived by metamorphic decarbonation reactions involving decomposition of carbonate minerals (Muffler and White, 1968; McKibben et al., 1993; McKibben and Williams, 1995). Subsurface mid-ocean

<sup>&</sup>lt;sup>a</sup>From Seward and Kerrick (1995).

ridge basalt (MORB) intrusions provide the heat for the geothermal systems. The localized intrusive heat sources, coupled with the development of calc-silicate hornfelses at depth (Bird et al., 1984) indicate that the deep sediments in the ST are undergoing contemporary thermal metamorphism. Advection of the hot fluids is controlled by the temperature-density balance of the fluids, which is unaffected by lithologic or stratigraphic features in the homogeneously fractured reservoir (A.E. Williams and McKibben, 1989). Surface expulsion of CO<sub>2</sub> is marked by warm springs and mud pots (Muffler and White, 1968).

The Salton Sea geothermal system (SSGS) provides a well-studied geothermal system within the ST (Fig. 2). In contrast to the conclusion of earlier studies, a carbonate caprock is absent in

the SSGS (A.E. Williams and McKibben, 1989; McKibben and Hardie, 1995; McKibben and Williams, 1995); consequently, there is no nearsurface barrier for transfer of dissolved CO2 from the convecting reservoir fluids to the overlying convecting groundwaters and, thus, to surface discharge sites. The identical C isotopic composition of CO<sub>2</sub> dissolved in the reservoir and CO<sub>2</sub> gas emitted by surface mud pots and hot springs affirms the open pathway of CO<sub>2</sub> flux to the surface (McKibben and Williams, 1995). Thus, convective CO<sub>2</sub> fluxes from the SSGS can be estimated from the measured convective heat flow and the temperatures and CO<sub>2</sub> contents of resfluids. Reservoir temperatures are ~300°C and fluid CO<sub>2</sub> contents are ~2000 mg kg<sup>-1</sup> (A.E. Williams and McKibben, 1989).

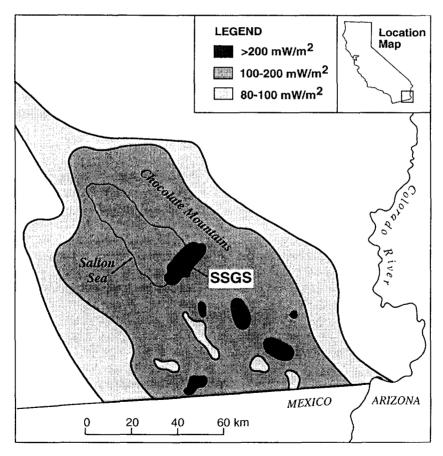


Fig. 2. Heat flow in the Salton Trough (modified from Lachenbruch et al., 1985). CO<sub>2</sub> flux was computed from the Salton Sea geothermal system (SSGS).

Based on enthalpy data for 25 eq wt% NaCl brines at 300°C (Phillips et al., 1981), fluid enthalpy is estimated to be  $\sim 1.0 \text{ kJ g}^{-1}$ . The SSGS exhibits anomalous heat flow ( $> 200 \text{ mW m}^{-2}$ ) over an area of ~200 km<sup>2</sup>; the mean heat flow within this area is  $\sim 450$  mW m<sup>-2</sup> (Lachenbruch et al., 1985; Sass et al., 1988). Using the mean heat flow, a total convective CO2 flux of  $10^8$  mol yr<sup>-1</sup> is estimated for the SSGS. This estimate is verified by a completely independent determination of the CO<sub>2</sub> flux (McKibben et al., 1993; McKibben and Williams, 1995). These authors documented the original mass of sedimentary carbonate in the system that had been lost to the atmosphere via metamorphism, coupling it with published radiometric ages for the system to derive an average CO<sub>2</sub> flux of 7·10<sup>8</sup>  $mol\ yr^{-1}$  over the lifetime of the system. Therefore, the heat-flow based estimate, which represents the present CO<sub>2</sub> flux of the mature decarbonated system, may underestimate the average CO<sub>2</sub> flux through time. The isotopic and chemical mass balance of McKibben and Williams (1995) indicates that the system can be viewed as undergoing "single-pass" convective circulation and in situ decarbonation. Any background contributions of CO<sub>2</sub> from deeper sources under the rift (mantle, MORB degassing) would be swamped by metamorphic CO<sub>2</sub> resulting from heating, brine advection and sediment decarbonation at shallow depths. As derived from the average CO<sub>2</sub> flux computed for a total area of 200 km<sup>2</sup>, a specific CO<sub>2</sub> flux of  $\sim 10^6$  mol km<sup>-2</sup> yr<sup>-1</sup> seems reasonable in light of available data for the SSGS. The total area of anomalously high heat flow in the ST is  $\sim 10$  times that of the SSGS field (Fig. 2). Assuming that the specific CO<sub>2</sub> flux from the SSGS ( $\sim 10^6 \text{ mol km}^{-2} \text{ yr}^{-1}$ ) is applicable to the entire high heat flow region in the Salton Trough, the total flux from the ST may be  $\sim 10^9 \text{ mol yr}^{-1}$ .

#### 4. Non-volcanic CO<sub>2</sub> emission in other areas

# 4.1. Circum-Pacific volcanic arcs

Many of the geothermal systems in the circum-Pacific are in subduction zone volcanic arc settings similar to the TVZ (Keller, 1982). As with the TVZ, isotopic and chemical data suggest that magmatically-derived volatiles are common in geothermal systems associated with circum-Pacific volcanic arcs (Giggenbach, 1992; Hedenquist, 1992; Reyes and Giggenbach, 1992). Accordingly, we use the CO<sub>2</sub> flux from the TVZ to estimate the CO<sub>2</sub> flux from other geothermal systems in volcanic arcs. More than 55 high-temperature geothermal systems occur in Indonesia (Ganda et al., 1992), and 30 occur in the Philippines (Reyes, 1990). Provisionally applying the total flux from the 20 known TVZ geothermal systems ( $\sim 10^{10}$  mol yr<sup>-1</sup>) to the 85 geothermal systems in Indonesia and Philippines, the total CO<sub>2</sub> flux from the southwest Pacific geothermal systems could be  $\sim 4 \cdot 10^{10}$  mol  $vr^{-1}$ . Considering the numerous other extensive geothermal systems within the circum-Pacific volcanic arcs (e.g., Japan and Central America), the flux of convective hydrothermal CO2 from circum-Pacific geothermal systems could be  $\sim 10^{11} - 10^{12} \text{ mol yr}^{-1}$ .

## 4.2. Northern California Coast Ranges

In addition to the ST, the north-central Coast Ranges of California represent another region where CO<sub>2</sub> may be dominantly of metamorphic origin (Irwin and Barnes, 1975). The upwelling mantle asthenosphere accompanying the formation of a slabless window (Furlong and Hugo, 1989; Donnelly-Nolan et al., 1993) has given rise to extensive recent extrusive and intrusive magmatic activity and associated high heat flow. There is considerable evidence for active metamorphism of the Franciscan complex at depth (Irwin and Barnes, 1975; Barnes et al., 1978, 1984; Furlong and Hugo, 1989; Stimac, 1993). Major faults provide conduits for the expulsion of CO<sub>2</sub> to the surface (Goff and Janik, 1993).

The Geysers geothermal system, which occurs in the high heat flow region of the north-central California Coast Ranges, produces more geothermal energy than any other geothermal field in the world, and ideally we could use the heat flow and reservoir CO<sub>2</sub> content of this system to estimate the CO<sub>2</sub> flux. Such an estimate would

appear to be of limited utility, however, for two reasons: (1) the Geysers geothermal system has undergone a natural transition in the recent geologic past from a liquid-dominated system to a vapor-dominated system (Donnelly-Nolan et al., 1993); and (2) the field has undergone extensive commercial exploitation and is drying out, resulting in changes in the reservoir steam compositions and pressures (Donnelly-Nolan et al., 1993). These natural and anthropogenic transitions have likely affected the enthalpy balance of the reservoir, such that any calculation of CO<sub>2</sub> flux based on the current heat flow and reservoir gas contents would be suspect in terms of its relevance to natural geologic CO<sub>2</sub> emission.

 $\rm CO_2$  springs are common in a broad area outside of the Geysers system (Irwin and Barnes, 1975). The  $\delta^{13}{\rm C}$  isotopic composition of the  $\rm CO_2$  emanating from these springs suggests that the  $\rm CO_2$  may originate from decarbonation of organic matter and/or decomposition of carbonate minerals within the Franciscan complex (Thompson et al., 1992).  $\rm CO_2$  springs are abundant within a  $6\cdot 10^3$ -km² area in the north-central Coast Ranges (Irwin and Barnes, 1975). With a specific  $\rm CO_2$  flux of  $\rm 10^6$  mol km $^{-2}$  yr $^{-1}$  derived for the TVZ and ST, the total  $\rm CO_2$  emission from the north-central Coast Ranges ( $\sim 10^{10}$  mol yr $^{-1}$ ) could be comparable to that of the TVZ.

## 4.3. Mediterranean Tethys

In addition to the circum-Pacific region, CO<sub>2</sub> springs are abundant within large areas of the Tethyan orogenic belt (Barnes et al., 1978, 1984). Geothermal systems in central Italy are particularly well documented (this includes the famous Lardarello geothermal system). CO<sub>2</sub> springs are abundant within a 3·10<sup>4</sup> km<sup>2</sup> area in the high heat flow region in central Italy (Minissale, 1991). Provisionally adopting the specific CO<sub>2</sub> flux of 10<sup>6</sup> mol km<sup>-2</sup> yr<sup>-1</sup> derived for the TVZ and ST yields a total CO<sub>2</sub> flux of ~3·10<sup>10</sup> mol yr<sup>-1</sup> for this region. Within the Mediterranean Tethys the map of Barnes et al. (1984) shows that CO<sub>2</sub> emission is abundant within an area of ~10<sup>6</sup> km<sup>2</sup>. With a specific CO<sub>2</sub> flux of

 $10^6$  mol km<sup>-2</sup> yr<sup>-1</sup>, the total CO<sub>2</sub> production in the Mediterranean Tethys could be ~ $10^{12}$  mol yr<sup>-1</sup>. Significant proportions of metamorphic CO<sub>2</sub> have been suggested for the Italian geothermal systems (Minissale, 1991), whereas mantle CO<sub>2</sub> has been suggested for other regions of the Mediterranean Tethys (Griesshaber et al., 1992; May et al., 1992). Regardless of the source, the Mediterranean Tethys could significantly contribute to the global atmospheric CO<sub>2</sub> budget.

## 5. Mantle vs. crustal CO<sub>2</sub> sources

High He<sup>3</sup>/He<sup>4</sup> isotopic ratios have been used to argue for a significant mantle derivation for He. However, He and CO<sub>2</sub> do not necessarily have the same origin (Matthews et al., 1987; O'Nions and Oxburgh, 1988; Griesshaber et al., 1992). In the SSGS, He, CO<sub>2</sub> and H<sub>2</sub>S emanating from mud pots have completely different origins: the He has  $R/R_a \sim 7$  (i.e. mantle signature), CO<sub>2</sub> is derived by metamorphism of crustal sediments, and H<sub>2</sub>S is of surface biogenic origin. Additional evidence for decoupling of volatile species is provided by the north-central California Coast Ranges where CO<sub>2</sub> springs along major fault zones have He isotopic data suggesting significant mantle derivation; however, the CO<sub>2</sub> isotopic compositions suggest a metamorphic origin (Goff and Janik, 1993). Furthermore, high He<sup>3</sup>/He<sup>4</sup> of magmatically-derived gases in volcanic arc geothermal systems does not necessarily imply that the CO2 is derived from the mantle (Giggenbach et al., 1993).

#### 6. Global implications

Quantification of global CO<sub>2</sub> emission from non-volcanic geothermal systems is hampered by the lack of data (heat flow and the temperatures and CO<sub>2</sub> contents of deep reservoir fluids) for many of these systems. If the specific CO<sub>2</sub> flux from these geothermal systems is similar to the TVZ and ST, the integrated non-volcanic CO<sub>2</sub> flux from all of the high heat flow areas could significantly contribute to atmospheric CO<sub>2</sub> con-

tent. Although unquantified, CO<sub>2</sub> emanating from tectonically active regions with low heat flow (Matthews et al., 1987; Giggenbach et al., 1991), and diffuse emission of magmatic CO<sub>2</sub> adjacent to volcanoes (Allard, 1992), will add to the atmospheric CO<sub>2</sub> content. Our computations suggest that non-volcanic CO<sub>2</sub> emission from high heat flow areas may substantially contribute to the CO<sub>2</sub> necessary to balance the global carbon cycle.

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